Preparation of Methacrylate End-Functionalized Poly(2-ethyl-2-oxazoline) Macromonomers

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Abstract
Three methods for the functionalization of 2-ethyl-2-oxazoline (EtOx) oligomers with a methacrylate or methacrylamide unit are compared to identify the best suitable route to obtain such macromolecules. In the first method, a functional initiator, namely methacryloyl chloride, was used for the cationic ring-opening polymerization of EtOx, which proceeded in a living manner. However, the formation of a large amount of hydrogen initiated chains resulted in a low degree of functionalization (21%). The second method was based on the termination of active oligo(EtOx) chains with an aqueous sodium carbonate solution yielding hydroxyl-terminated oligomers. These end-groups were subsequently modified by an esterification reaction with methacryloyl chloride yielding oligomers with a large variety of different end-groups, as demonstrated by MALDI-TOF-MS. In the last method, the living chain ends were reacted with \textit{in situ} formed triethyl ammonium methacrylate yielding macromonomers with a high degree of functionalization (>80%). Besides, MALDI-TOF-MS analysis revealed only a single oligomer distribution with the desired end-groups. Furthermore, these directly end-capped oligomers revealed narrow molar mass distributions with PDI values below 1.2 making this the best method for macromonomer synthesis.

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Keywords
Poly(2-ethyl-2-oxazoline), MALDI-TOF-MS, end-functionalization, living polymerization, macromonomer

1. Introduction
The cationic ring-opening polymerization (CROP) of 2-oxazolines [1–6] proceeds in a living manner under appropriate conditions [7, 8]. A cationic species is formed by utilizing a suitable electrophilic initiator, which is prone to undergo attack the nitrogen atom of the oxazoline ring. The formed oxazolinium species is capable

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to add further monomers, resulting in chain propagation until all monomer is consumed. In such an ideal case, this living mechanism leads to polymers with defined end-groups, one of which is the initiator moiety and the other one is the oxazolinium species that can be terminated by the addition of a nucleophile. The detailed mechanism of this polymerization is shown in Scheme 1.

The polymerization of 2-oxazolines can be accelerated by increasing the reaction temperature as long as no side-reactions are induced [9–11]. The use of microwave irradiation provides the possibility of fast heating and accurate temperature control, even in cases where the reaction mixture is heated above the boiling point of the solvent [12–15].

Although a variety of 2-oxazoline monomer units has been prepared and polymerized in a living manner, the combination of 2-oxazolines with other vinylic monomers would further enhance the versatility of this class of polymers. To allow the combination of poly(2-oxazoline)s with vinylic monomers, the use of methacrylate functionalized poly(2-oxazoline)s seems to be ideally suited. There are already three different routes reported for the preparation of methacrylate functionalized poly(2-oxazoline)s, as outlined in Scheme 2.

On the one hand, it might be possible to use a functionalized initiator [16, 17], while, on the other hand, the living cationic chain end can be terminated by nucleophiles, containing a methacrylate or another functional group that can be transformed into a methacrylate [18–21].

In our previous work, we have demonstrated the use of various acetyl halides as initiators for the CROP of EtOx [22, 23]. Similarly, the utilization of methacryloyl chloride as initiator [24] for this reaction should provide an oligo(2-ethyl-2-oxazoline) (OEtOx) chain with one methacrylate end-group and a remaining living second chain end for further functionalization reactions (see Scheme 2). This synthetic strategy was successfully realized by Dworak [24] to obtain macromonomers from 2-methyl-2-oxazoline (MeOx) and 2-phenyl-2-oxazoline (PhOx). Moreover, the polymerization of EtOx has been initiated with vinyl iodoacetate providing macromonomers having a vinyl ester end-group with an almost quantitative degree of functionalization [17].

There are several possibilities for the end-group functionalization of poly(EtOx) with a methacrylate unit when the polymerization is initiated with a standard non-functionalized initiator like methyl tosylate. It is known that a hydroxyl-terminated PEtOx can be obtained by end-capping the living polymer chain with an aqueous
Scheme 2. Schematic representation of the different routes to synthesize oligo(EtOx) methacrylate macromonomers.

solution of potassium hydroxide or sodium carbonate [19]. Subsequently, functionalization of the alcohol with methacryloyl chloride leads to the methacrylate macromonomers [19, 21] (see Scheme 2).

Due to the fact that the polymerization of EtOx proceeds cationically, it is also possible to terminate the cationic species directly with a methacrylate anion. Such a desired anion can easily be formed by the deprotonation of methacrylic acid with a suitable base, either triethyl amine [19] or the more sterically hindered lutidine [20]. This method has already been used to obtain methacrylate functionalized MeOx oligomers [20], as well as acrylate-functionalized EtOx oligomers [19].
In the current study, we compare and discuss the advantages and disadvantages of the three different synthetic strategies for the preparation of poly(EtOx) macromonomers providing detailed characterization data based on matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. The use of MALDI-TOF-MS allows the accurate detection of the specific end-groups of the polymers [25] and, therefore, provides an excellent basis for the evaluation of the prepared macromonomers.

2. Experimental

2.1. Materials

2-Ethyl-2-oxazoline (EtOx, 99%, Acros) was dried over barium oxide and distilled under argon prior to use. Methyl tosylate (MeTos, 98%, Aldrich) was distilled and stored under argon. Acetonitrile (extra dry, Acros) was stored under argon. Methacrylic acid (MAA, 99%, Aldrich) and methacryloyl chloride (MACl, 97%, Fluka) were used as received. Triethyl amine was dried over potassium hydroxide and distilled under argon. Methylene chloride was dried over molecular sieves and distilled under argon.

2.2. Instrumentation

$^1$H-NMR spectra were recorded on a Bruker AC 250 MHz using the residual solvent resonance as an internal standard. Gel-permeation chromatography (GPC) was measured on a Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump and a RID-10A refractive index detector using a solvent mixture containing chloroform, triethylamine and isopropanol (94:4:2) at a flow rate of 1 ml/min on a PSS-SDV-linear M 5 µm column at room temperature. The system was calibrated with polystyrene (0.37–67.5 kDa) standards. For the measurement of the matrix-assisted laser desorption/ionization (MALDI) spectra an Ultraflex III TOF/TOF (Bruker Daltonics) was used. The instrument was equipped with a Nd:YAG laser and a collision cell. All spectra were measured in the positive reflector mode with dithranol as matrix and sodium iodide as salt. The instrument was calibrated prior to each measurement with an external PMMA standard from PSS Polymer Standards Services. For the polymerization of EtOx an oilbath or a Biotage Initiator Sixty microwave synthesizer was used under temperature-control (IR-sensor; accuracy within 1°C).

2.3. Polymerization of 2-Ethyl-2-oxazoline Initiated by Methacryloyl Chloride

Methacryloyl chloride (0.155 g, 1.48 mmol), EtOx (2.798 g, 28.2 mmol) and acetonitrile (3.32 g) were mixed under inert conditions. The concentration of EtOx was kept at 4 mol/l and the monomer to initiator ratio at 20:1. Into each pre-dried microwave vial (kept at 110°C overnight and cooled under argon) 0.5 ml of this stock solution were transferred under inert conditions. The capped vials were heated to
90°C in an oil bath for 16 h, 26 h or 40 h in order to follow the reaction kinetics. The polymerization was quenched by addition of a drop of water into the vial. The reaction mixture was dissolved in chloroform and purified by precipitation into cold hexane. $^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ 5.66 (═CH$_2$), 5.30 (═CH$_2$), 4.27 (m, CH$_2$—COO), 3.44 (m, N—CH$_2$); 3.02 (m, N—CH$_3$), 2.35 (m, C—CH$_2$—C), 1.92 (m, CH$_2$═C—CH$_3$), 1.12 (m, C—CH$_3$).

2.4. Polymerization of 2-Ethyl-2-oxazoline Initiated by Methyl Tosylate in the Microwave Synthesizer

Methyl tosylate (2.490 g, 13.4 mmol), EtOx (3.971 g, 40.1 mmol) and acetonitrile (6.0 ml) were transferred to pre-dried microwave vials under inert conditions. In all cases the concentration of EtOx was kept at 4 mol/l. The amounts of methyl tosylate and EtOx were calculated according to the desired monomer to initiator ratio. The vials were capped with suitable septa and placed in the autosampler of the microwave. After 10 s of pre-stirring, the reaction solution was heated to 140°C and the temperature was held for the desired reaction time (1–5 min, depending on the monomer to initiator ratio). Subsequently, the vial was cooled to room temperature under a nitrogen flow. For the polymerizations in 0.5–2 ml vials, the absorption level was set to normal whereas it was set to very high when 20 ml vials were used in order to reduce the thermal overshoot in the heating profile.

2.5. End-Capping of Living Oligo(2-ethyl-2-oxazoline) with Water in the Presence of Sodium Carbonate

The reaction solution containing the living oligo(EtOx) chains (see Section 2.4; 3.28 mmol) was added to a solution of 1.27 g (23 mmol) sodium carbonate in 10 ml water. This mixture was stirred overnight at 90°C and extracted three times with chloroform after cooling to room temperature. The combined organic phases were dried over sodium sulfate and filtered. Finally, the solvent was evaporated under reduced pressure and the white sticky polymer was dried under reduced pressure. $^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ 3.44 (m, N—CH$_2$); 3.02 (m, N—CH$_3$), 2.35 (m, C—CH$_2$—C), 1.12 (m, C—CH$_3$).

2.6. Esterification of the Hydroxyl-Terminated Oligo(2-ethyl-2-oxazoline)

Hydroxy-terminated oligo(EtOx) (A4, 0.5 g, 0.25 mmol) and triethyl amine (0.09 g, 0.89 mmol) were dissolved in 10 ml dry methylene chloride. Afterwards, a solution of methacryloyl chloride (0.059 g, 0.56 mmol) in 3 ml dry methylene chloride was added dropwise. After 24 h, 3 ml saturated aqueous sodium hydrogen carbonate solution was added. The mixture was stirred for 4 h before it was extracted three times with methylene chloride. The combined organic phases were dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The resulting white polymer (E1, 0.313 g) was dried under reduced pressure. $^1$H-NMR (250 MHz, CDCl$_3$): $\delta$ 5.00–6.20 (4 peaks, =CH$_2$), 4.27 (m, CH$_2$—COO), 3.44 (m, N—CH$_2$); 3.02 (m, N—CH$_3$), 2.35 (m, C—CH$_2$—C), 1.92 (m, CH$_2$═C—CH$_3$), 1.12 (m, C—CH$_3$).
2.7. End-Capping of Living Oligo(2-ethyl-2-oxazoline) with Methacrylic Acid

Methacrylic acid (1.7 ml, 20 mmol) was added in 1.5-fold excess via a syringe through the septum of the capped microwave vial containing the solution of living oligo(EtOx) (see Section 2.4; 13 mmol). Thereafter, triethyl amine (3.7 ml, 26.7 mmol) was added similarly in a two-fold excess. The given amounts were varied according to the used monomer to initiator ratios. The reaction solution was heated to 80°C for 15 h. The acetonitrile was evaporated and the polymer was redissolved in chloroform. This solution was washed with saturated aqueous sodium hydrogen carbonate and saturated brine, dried with sodium sulfate and filtered. The solvent was evaporated under reduced pressure and the resulting white polymer was dried under vacuum and stored at −18°C under argon.

$^{1}H$-NMR (250 MHz, CDCl$_3$): δ 6.07 (−CH$_2$), 5.58 (−CH$_2$), 4.27 (m, CH$_2$–COO), 3.44 (m, N–CH$_2$); 3.02 (m, N–CH$_3$), 2.35 (m, C–CH$_2$–C), 1.92 (m, CH$_2$=C–CH$_3$), 1.12 (m, C–CH$_3$).

3. Results and Discussion

The synthesis of methacrylate-functionalized oligo(EtOx) was investigated using three different synthetic strategies as depicted in Scheme 2. The first route is based on initiating the polymerization of EtOx with methacyloyl chloride. The second route (esterification) consists of two steps, namely the synthesis of hydroxyl-terminated EtOx oligomers and their subsequent esterification with methacyloyl chloride. Finally, living oligo(EtOx) chains can be terminated with deprotonated methacrylic acid using the direct end-capping route.

3.1. Methacyloyl Chloride-Initiated Polymerization of EtOx

The initiation route was evaluated by performing a kinetic study of the polymerization of EtOx at 90°C initiated with methacyloyl chloride. The molar masses and PDI values were determined by GPC using polystyrene calibration. The conversion of the monomer was calculated from the integrals of the methylene peaks in the $^{1}H$-NMR spectrum (CDCl$_3$) belonging to the ring in the monomer (4.21 ppm and 3.75 ppm) and the backbone (3.44 ppm) in the polymer, respectively. In addition, the $^{1}H$-NMR spectra revealed the presence of vinylic protons in the reaction solution demonstrating the preservation of the unsaturated methacrylamide functionality at 90°C.

The relatively low PDI values (mainly below 1.2) together with the linear increase of $M_n$ values with conversion and the linear semi-logarithmic kinetic plot suggest a living polymerization (see Fig. 1). Nonetheless, the GPC traces show a shoulder on the high molar mass side indicating coupled chains (Fig. 2). This chain coupling arises probably due to the relatively high conversion (87%) after a polymerization time of 26 h.

The final polymer I1 was precipitated into hexane and further characterized by GPC (CHCl$_3$, see Fig. 2), $^{1}H$-NMR spectroscopy (CDCl$_3$, see Fig. 3) and MALDI-TOF mass spectrometry. The GPC trace of the polymer was unaffected by the
Figure 1. Kinetic plots for the polymerization of EtOx initiated with methacyryloyl chloride at 90°C.

Figure 2. GPC traces (CHCl₃) of oligo(EtOx) initiated with methacyryloyl chloride.

Figure 3. ¹H-NMR spectrum (250 MHz) in CDCl₃ of oligo(EtOx) I initiated by methacyryloyl chloride. (——) Precipitated polymer, (-----) reaction solution.
precipitation (Fig. 2). Although the $^1$H-NMR spectrum of the precipitated polymer displays the expected peaks of an oligo(EtOx), the vinylic proton signals significantly decreased compared to the spectrum of the reaction solution. A degree of functionalization of only 21% was calculated from the integrals of these peaks indicating a significant amount of chain transfer during the polymerization.

The occurrence of chain transfer-reactions is supported by the main distribution observed in the MALDI-TOF-MS (see Fig. 4, structure 1), which corresponds to an oligo(EtOx) structure with a hydrogen end-group instead of the expected methacrylamide. The chain transfer mechanism leading to hydrogen initiated chains will be discussed in the following part of this contribution. Nevertheless, the desired distribution with a methacrylamide end-group could also be observed in the MALDI-TOF mass spectrum (Fig. 4, structure 2).

Although the initiation with a methacrylate bearing initiator would be beneficial for further functionalization of the living oligo(EtOx) chain ends, the occurrence of chain transfer reactions makes this route unsuitable for a subsequent radical polymerization of the macromonomers. Future research might be directed to decreasing

![Figure 4. MALDI-TOF-MS of an oligo(EtOx) initiated by methacryloyl chloride. (A) Full spectrum; (B) zoom into the region m/z 2100–2230 and schematic representation of the proposed structures corresponding to the signals (top).](image)

the amount of chain transfer by lowering the reaction temperature, performing the polymerization until lower conversions or by changing the counter ion to a more reactive one such as iodide.

3.2. Two-Step Post-Polymerization Modification

Well-defined oligo(EtOx) can be obtained by polymerizing EtOx using methyl tosylate as initiator for the cationic ring-opening polymerization of EtOx at 140°C in a microwave reactor [13]. Due to the fact that the polymerization has a living character the chain length can be easily controlled by using different monomer to initiator ratios. Thus, the obtained living polymer chains can be terminated with water leading to the formation of a hydroxyl terminated oligo(EtOx) (OEtOxOH). As known from the literature [19], the alcohol is formed as the thermodynamically favoured product during a rearrangement of an ester structure, which is reported to be the kinetically favoured product. Using this synthetic procedure well-defined hydroxyl-functionalized EtOx oligomers were synthesized with varying degrees of polymerization (for GPC traces see Fig. 5).

In a second step, the alcohol of oligo(EtOx) A4 was reacted under basic conditions with methacryloyl chloride, leading to the desired oligo(EtOx) methacrylate (OEtOxMA) macromonomer E1. Analysis by GPC (see Fig. 5) shows that the polymer chains do not undergo coupling reactions during the end-group modification.

The end-group modification of the oligomer was evaluated by comparison of the $^1$H-NMR spectra of the OEtOx alcohol (A4) and the corresponding methacrylate (E1) (Fig. 6). The spectrum of the alcohol shows a shoulder next to the peak of the polymer backbone at 3.6 ppm, which belongs to the methylene protons next to the hydroxyl group of the OEtOxOH. The appearance of a peak at 4.3 ppm in the spectrum of the OEtOxMA indicates that there are methylene protons next to an ester function. A degree of substitution of 50% can be calculated from the integrals of the appearing peaks belonging to the vinylic protons.

![Figure 5. GPC traces (CHCl$_3$) of OEtOx-OH and OEtOxMA initiated with MeToS.](image-url)
In addition, the synthesized oligomers were characterized by MALDI-TOF-MS revealing that there are several distributions with a mass difference of 99 Da between the peaks present in all of the samples. A typical MALDI spectrum of an OEtOxOH, where the distributions were assigned to possible end-groups of polymer A2, is shown in Fig. 7.

The observed main distribution fits to the desired structure of an OEtOx chain with a methyl and a hydroxyl end-group. The two minor distributions can be explained by known chain transfer reactions which take place during the polymerization of oxazolines [26] leading to hydrogen-initiated chains (difference of 14 Da, peak 3 in Fig. 7) on the one hand and to an enamine structure on the other hand. As shown in Scheme 3A, the latter can react with water during the end-capping procedure resulting in a structure fitting to the distribution numbered as 2 in Fig. 7. An alternative chain-transfer mechanism which is based on the presence of H-nucleophiles can provide an explanation for the observed structures as well (Scheme 3B) [27]. Traces of water as H-nucleophiles can attack the oxazolinium species under formation of hydroxyl terminated low molar mass chains. The occurring second product, toluene sulfonic acid, can provide protons to attack a present EtOx monomer and to start a new, hydrogen initiated polymer chain (structure 3 in Fig. 7). The appearance of structure 2 (Fig. 7) can also be a result of the large excess of sodium carbonate used during the end-capping procedure. The activated oxazolinium end-group can be attacked by hydroxyl anions in an analogue way to a saponification reaction of an ester under too basic conditions. The already formed amide structures of the polymer chain are more stable than the already positively charged and, thus, activated end moiety of the oligomer under such basic conditions.

Unfortunately, the impurities in the OEtOxOH resulting from chain-transfer reactions during the polymerization contain –NH– functions. These secondary amines
can be attacked by methacryloyl chloride during the esterification step as well as the OH-function of the alcohol. The occurrence of these side-reactions is supported by the MALDI-TOF mass spectrum of the OEtOxMA synthesized by the esterification route which, indeed, shows a variety of mono- and bimethacrylate functionalized macromonomers (see Fig. 8).

According to the characterization results obtained for the synthesized macromonomer by $^1$H-NMR spectroscopy and MALDI-TOF mass spectrometry, the esterification route seems to be not a feasible way to obtain well-defined macromonomers as long as the chain transfer reactions during the polymerization of the EtOx cannot be totally suppressed. Occurring chain-transfer reactions during the polymerization of EtOx lead to –NH– functions in the polymer, which offer a second position for an attack of methacryloyl chloride. As a consequence, some of the resulting monomers contain two methacrylate moieties and can cause cross-linking during a subsequent radical polymerization process.

3.3. Direct End-Capping of the Living Chains with Methacrylic Acid

EtOx was polymerized in the microwave synthesizer at 140°C using methyl tosylate as initiator and acetonitrile as solvent for the direct end-capping method. The living chains were terminated by in situ formed triethyl ammonium methacrylate, which
was achieved by addition of methacrylic acid and triethyl amine to the reaction solution. Using this method a series of well-defined oligo(EtOx) methacrylates with varying degrees of polymerization was synthesized, which were characterized by GPC, $^1$H-NMR spectroscopy and MALDI-TOF mass spectrometry.

The macromonomers show narrow molar mass distributions without any shoulders in their GPC traces (see Fig. 9). The shoulders of the GPC trace of the shortest macromonomer $M_1$ are most likely caused by separation of the different monodisperse fractions on the column.

The degree of polymerization was calculated from the signals of the aromatic hydrogen atoms belonging to the counter ion (tosylate) and the peak of the polymer backbone in the $^1$H-NMR spectrum of the reaction solution (see Fig. 10).
Figure 8. MALDI-TOF-MS of oligo(EtOx) methacrylate E1 prepared via the esterification route. (A) Full spectrum; (B) zoom into the region $m/z$ 2195–2310 and schematic representation of the proposed structures corresponding to the signals (top).

Figure 9. GPC traces (CHCl$_3$) of oligo(EtOx) methacrylates M1–M7 obtained by the direct end-capping route.

addition, the degree of functionalization can be calculated from the integrals of the peaks of the vinylic protons of the methacrylate in comparison to the tosylate signals (labeled as 1 in Fig. 10). The excess of base, methacrylic acid and the tosylate
was removed during the purification of the crude product by several extraction steps with chloroform yielding pure OEtOxMA macromonomers.

MALDI-TOF-MS analysis was performed to further identify the structure of the macromonomers prepared by direct end-capping. The obtained mass spectra of the purified macromonomers (see Fig. 11) revealed only a single polymer distribution. The masses of the corresponding peaks fit to an OEtOx structure with both methyl and methacrylate end-groups and have a distance of 99 Da, which is the molar mass of one monomeric unit. It should be noted that each species is ionized by a sodium cation.

A series of well-defined oligo(EtOx) methacrylates with high degrees of functionalization could be obtained by this direct end-capping method. The characterization data of the synthesized oligomers are summarized in Table 1. Even though it is not possible to obtain quantitative functionalization, the remaining polymer chains most likely resulting from chain-transfer reactions will not bear the methacrylate functionality and will not interfere with subsequent radical polymerizations.

4. Conclusion

Well-defined oligo(EtOx) methacrylates could be only obtained by the direct end-capping of living oligo(EtOx) chains with in situ formed triethyl amino-
Figure 11. MALDI-TOF-MS of an oligo(EtOx) methacrylate obtained by the direct end-capping route. (A) Full spectrum of M1, (B) zoom into the region m/z 610–725.

Table 1.
Structural characterization of the oligo(EtOx) methacrylates

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<th>Oligomer</th>
<th>[M]/[I] calcd. a</th>
<th>DP (1H-NMR) b</th>
<th>F (1H-NMR) c</th>
<th>$M_n$ d (g/mol)</th>
<th>PDI d</th>
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a Calculated from the amount of monomer and initiator used.
b Calculated from the aromatic signals of the initiator and the methylene signals of the polymer backbone.
c Calculated from the vinylic protons of the end-group and the methylene signals of the polymer backbone.
d Obtained from GPC using polystyrene calibration.

### Discussion

This route could be used for the preparation of a range of macromonomers with different chain length and a functionality higher than 80%. The initiation route using methacryloyl chloride as initiator for the polymerization of EtOx yielded very low (20%) functionality due to chain-transfer reactions. Fur-
thermore, the introduction of a hydroxyl group in the poly(2-oxazoline) followed by esterification with methacryloyl chloride yielded a wide range of end-groups, including bifunctional acrylates, that will act as cross-linker in subsequent radical polymerization procedures. MALDI-TOF-MS proved to be an excellent tool to determine the end-groups of such macromonomers allowing a better understanding of the reactions.

The successful synthesis of OEtOxMA opens a way towards new comb-shaped polymer architectures with hydrophilic OEtOx side-chains by the use of the macromonomer method making the poly(2-oxazoline)s available to a much broader community. The biocompatibility and stealth properties of poly(EtOx)s [28] make such macromonomers interesting precursors for biologically relevant materials. Current investigations are directed to the controlled radical polymerization of such OEtOxMA macromonomers.

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